The University of Chicago

I. AN ATTEMPT AT ENZYMATIC AROMATIZATION IN VITRO

II. STUDIES IN THE SYSTEM, LANTHANUM-HYDROGEN

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
1939

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HERMAN SCHNEIDERMAN

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ACKNOWLEDGMENT

The author wishes to express his appreciation to Dr Thorfin Hogness and Dr. Albert Sidwell for their patient guidance throughout the first portion of this investigation and to Dr. Warren C. Johnson, who suggested the second problem and gave helpful assistance throughout its investigation. To Dr. Lyle Hill, the author is indebted for kindly discussion of the second portion of this work.

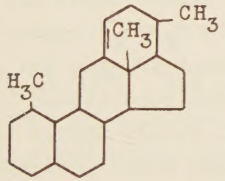
The author also wishes to thank the Educational Alliance of New York City, the College of the City of New York, and the Department of Chemistry of the University of Chicago for grants in aid.

AN ATTEMPT AT ENZYMATIC AROMATIZATION IN VITRO

Introduction

The similarity between a number of the carcinogenic hydrocarbons and naturally occurring sterols suggests a possible relation between the occurrence of cancer and pathological biosynthesis of the sterols. A major source of circumstantial evidence lies in the non-carcinogenic action of many hydrogenated compounds and the appearance of carcinogenic activity on dehydrogenation. Thus, dehydronorcholene (I), a compound obtainable from naturally occurring bile acids, has no carcinogenic activity, but its dehydrogenated product, methylcholanthrene (II), has considerable carcinogenic potency.[1] While many examples of the preparation of carcinogenic compounds from biologically important antecedents may be cited, it has yet to be demonstrated that these changes actually take place in the animal system.

I.



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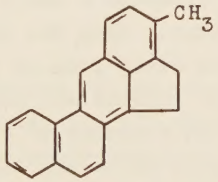

In 1911, Friedmann[2] conducted feeding experiments on dogs, using simple cyclic compounds. This work has been repeated and extended by Bernhard.[3] Hexahydrobenzoic acid, the methylamide and dimethylamide of hexahydrobenzoic acid, hexahydrohippuric acid, and cyclohexyl propionic acid were administered and each resulted in an increase in the hippuric acid content of the dog's urine. Amongst others, cyclohexanol, methyl cyclohexane, and dimethylcyclohexane

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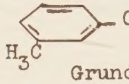
[1] Wieland and Dane, Z. physiol. Chem., 219, 240 (1933).

[2] Friedmann, Biochem. Z., 35, 48 (1911).

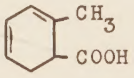
[3] Bernhard, Z. physiol. Chem. 248, 256 (1937).

did not result in an aromatized product. The cis and trans hexahydro-ortho-toluic acids were excreted unchanged, whereas hexahydro-meta-toluic acid yielded some of the aromatized product

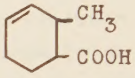


Grundmann[1] reported that o-dihydrotoluic acid (III) is transformed into o-toluic acid. The feeding of Δ^5 tetrahydro-o-toluic acid (IV) yielded no dehydrogenated product.

III.



IV.



These in vivo experiments pointed to the use of the readily available cyclohexane carboxylic acid as a starting point for a study of the possible existence of an aromatizing enzyme.

Experimental

Fresh liver, kidney, and pancreas of a dog were immediately placed in a Dewar container filled with dry ice. The extracts were made by grinding a small piece of frozen tissue under dry ice to a fine powder. This was extracted with M/10 K_2HPO_4 (approximately 4 cc. for every gram of tissue). After centrifuging the mixture at 3°C., the supernatant pipettable suspension constituted the "enzyme." In a number of other experiments, finely minced tissue was washed with water and then ground with sand under phosphate buffer. This mixture was then strained through linen and the filtrate was used.

The dehydrogenase activity was measured by the Thunberg method, which depends on the rate of decolorization of a dye. A measured amount of dye solution, a phosphate buffer having a pH of 7.2 and a water solution of the substrate were placed in the tube (Figure 1). The ratio of the substrate to the dye was at least one hundred to one. The tissue extract was placed in chamber A . The ground glass joint was greased and after the tube was evacuated, chamber A was turned to give an air-tight system. The contents were mixed thoroughly and the tubes were then shaken in a

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[1]Grundmann, Z. angew. Chem., 51, 405 (1938).

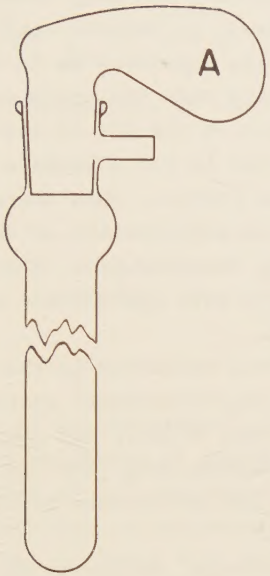

Fig. 1

water bath at 37°C. The rate of decolorization of the dye was compared to that in a control (i.e. a tube containing all components except the substrate). The reaction may be represented as:

$$\text{Substrate} + \text{Dye} \xrightarrow{\text{Enzyme}} (\text{Substrate} - H_2) + \text{Leuco-dye}$$

Twice vacuum distilled cyclohexane carboxylic acid, having a melting point of 30° and a boiling point of 114° at 9 mm., was used. When the acid was dissolved in alkali to give a 0.2 M solution, opalescent solutions were occasionally obtained. Further addition of alkali did not result in a clear solution. In some cases, clear solutions were obtained at first, but globules of immiscible liquid appeared after a few days. For no apparent reason, stable solutions were sometimes obtained. Such solutions were tested with buffered 2,6 dichlorophenol indophenol in Thunberg tubes and no decolorization was observed.

In the use of liver extracts prepared according to the methods described, a marked decolorization of the dye in the

presence of the cyclohexane carboxylic acid solution led to the belief that some dehydrogenation was taking place. However, the results were not reproducible, and when o-chlorophenol, a dye of higher potential was used, it was not readily decolorized. This anomaly, coupled with the questions as to whether a completely homogeneous solution resulted when the cyclohexane carboxylic acid was dissolved in alkali, led to the use of solutions of cyclohexane carboxylic acid dissolved in 7.2 phosphate buffer and of dyes dissolved in 7.2 phosphate buffer. When these solutions were tested with liver extracts, the acceleration of the loss of color of the dye could not always be demonstrated. Kidney and pancreas extracts yielded negative results with cyclohexane carboxylic acid solutions prepared in either way.

An experiment was conducted in the Warburg Apparatus to determine the effect of the cytochrome[1] system. Cyclohexane carboxylic acid solutions, liver, kidney, and pancreas extracts (prepared by grinding the fresh tissue under dry ice) were shaken in the presence of cytochrome and cytochrome oxidase. No dehydrogenase activity was indicated.

The cyclic compounds, cyclohexanol, cyclohexanone, Δ^2 cyclohexenol,[2] and Δ^2 cyclohexenone were also investigated. (These groups are present in sex hormones.) Thunberg tests of each of these compounds with extracts of fresh liver, pancreas, and kidney, showed no action.

Preparation of Δ^2 cyclohexenone.--Much difficulty was encountered in the preparation of Δ^2 cyclohexenone and some doubt remains as to the purity of the compound finally used in one of the above attempts at aromatization. The following discussion is presented in order that the person who continues this work may be guided by it.

The close resemblance of the enol form of Δ^2 cyclohexenone to phenol would lead one to expect this compound to be particularly susceptible to aromatization. In connection with this expectation, it is interesting to note the transformation of ketotetrahydrobenz-

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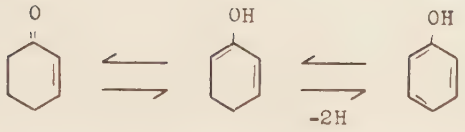
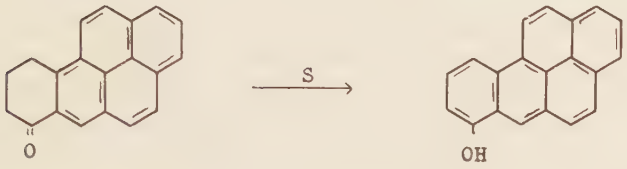
[1]The dehydrogenases and their substrates reduce cytochrome, which is then reoxidized by combining with oxygen in the presence of the oxygen-activating cytochrome oxidase.

[2]This compound is difficultly soluble in water, but it was possible to prepare a .01 M water solution.



pyrene to 4'-hydroxy-1,2-benzpyrene by the use of sulphur.[1]



The bromination of cyclohexanone[2] with consequent removal of hydrogen bromide, the oxidation of cyclohexene with selenium dioxide[3] and the oxidation of Δ^2 cyclohexenol[4] are the three most feasible methods of preparing cyclohexenone. The objection to the bromination method was the ease with which brom-cyclohexanone polymerizes. The use of selenium dioxide was undesirable because of the polymerizing effect of the resulting selenium.

Δ^2 Cyclohexenol was prepared according to the method of Hofmann and Damm.[5] 1,2 Dibromocyclohexane was refluxed with potassium acetate and glacial acetic acid to give cyclohexenyl acetate which, after hydrolysis, yielded Δ^2 cyclohexenol. This compound had a boiling point of 63° at 11 mm., a refractive index of 1.4860 (21°) and a urethane which melted at 107°. When the directions of Kotz and Richter[6] were used to prepare the Δ^2 cyclohexenone by dichromate oxidation, no Δ^2 cyclohexenone was obtained. These workers stated that the oxidation mixture should be steam

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[1]Fieser, Hershberg, and Newman, J.A.C.S., 57, 1509 (1935).

[2]Kötz and Grethe, J. Prkt. Chem., 80, 488 (1909).

[3]Guillemonat, Compt. rend., 205, 67 (1938).

[4]Kötz and Richter, J. Prkt. Chem., 111, 398 (1925).

[5]Hofmann and P. Damm, Mitt. schlesischen Kohlen forschungsinst. Kaiser-Wilhelm-Ges. 2, 97 (1925).

[6]Kötz and Richter, op. cit.

distilled and after ether extraction of the distillate, the extract should be dried over calcium chloride. Δ^2 Cyclohexenone is soluble in water and it is difficult to understand how the authors could steam distil the compound and obtain a seventy per cent yield. Courtot and Pierron[1] obtained Δ^2 cyclohexenone by heating chlorcyclohexene with dichromate oxidizing mixture at 60°, and direct extraction with ether.

This modification (heating to 60°) was adapted to Δ^2 cyclohexenol, and the resulting ketone readily formed a semicarbazone which, after recrystallization, melted at 161°. Unfortunately, the ketone thus obtained was yellow throughout distillation and subsequent redistillations in a nitrogen atmosphere did not remove the color. Attempts to decolorize the compound by shaking it with charcoal or alumina were unsuccessful.

Compounds like Δ^2 cyclohexenone are extremely susceptible to polymerization in the presence of alkali, peroxides, and light. Suitable provision for the elimination of these variables has not been made in previous methods. The following method was devised to yield a colorless compound which remained colorless in water solution for four months.

To a well stirred emulsion of 15 g. of Δ^2 cyclohexenol dissolved in 225 cc. of water containing 18.5 g. of potassium dichromate was added a solution of 30 g. of concentrated sulphuric acid in 50 cc. of water over a period of half an hour. The mixture was then kept at 50-55° for one and one-half hours. After cooling the reaction mixture, it was almost completely neutralized with dilute sodium hydroxide, and saturated with sodium sulfate. A zone of brown liquid appeared at the top. The mixture was steam distilled, the distillate was separated from a small lower layer of unoxidized Δ^2 cyclohexenol, and finally filtered through filter paper to remove small globules. The distillate was saturated with sodium sulfate, washed with a saturated solution of sodium sulfate containing a small amount of dipotassium acid phosphate, extracted with anhydrous ether, and dried over sodium sulfate. After evaporating the ether, the residue was distilled in vacuum, with the receiver immersed in a suspension of solid carbon dioxide in chloroform. The distilling bulb was warmed slightly to start distillation and a very slow rate of distillation was maintained. The

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[1] Courtot and Pierron, Bull. Soc. Chim., 45, 286 (1929).

middle, colorless fraction thus obtained was redistilled twice more in the same manner.[1] When the purified Δ^2 cyclohexenone was dissolved in previously boiled distilled water and the bottle painted with optical black, the solution remained colorless.

After this solution was added to a number of dyes in Thunberg tubes, all were decolorized except one. The dyes decolorized were o-chlorophenol, 2,6 dichlorophenol indophenol, 1-naphthol-2-sulfonate 2,6 dichlorophenol indophenol, indigo, di-, tri-, and tetra-sulfonate. There was no loss of color when 1-naphthol-2-sulfonate indophenol was used.

The decolorization of the dye, as a result of direct interaction with Δ^2 cyclohexenone, may be considered to be an oxidation-reduction process in which the Δ^2 cyclohexenone donates hydrogen atoms to the dye and is in itself oxidized to phenol. If this interpretation is true, it is difficult to understand why acid dichromate, used in the oxidation of Δ^2 cyclohexenol, does not change the resulting cyclohexenone to phenol. It is a well substantiated assumption that the transformation of colored dye to leuco dye is the result of reduction via the acceptance of two hydrogen atoms by a conjugated system. However, Δ^2 cyclohexenone contains a conjugated system which is very apt to react by condensation. It is possible that the decolorization is due to a condensation with the conjugated system of the dye. Any interpretation would be speculative rather than conclusive, and the subject requires more laboratory investigation.

The cyclohexenone group is of much biological importance and the clarification of its action may prove of practical value. The following suggestions are therefore made for the continuation of the problem: (1) A synthesis of Δ^2 cyclohexenone should be developed by cyclization of a straight chain compound. This synthesis should eliminate the oxidation of the Δ^2 cyclohexenol to the ketone. (2) The equilibrium between the keto and enol forms of Δ^2 cyclohexenone at various temperatures and in 7.2 phosphate buffer should be determined. (3) A more detailed investigation of dye-

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[1] $n_D^{21} = 1.4842$. The value of Guillemonat (Compt. rend. 205, 67 [1938]) is 1.4741. Since a semicarbazone gave the proper melting point of 161°, and above all, the solution remained colorless, no further attempt was made to check the index of refraction previously recorded.

cyclohexenone interaction should be undertaken in order to establish the potential of the Δ^2 cyclohexenone-phenol system. (4) Substituted cyclohexenones and compounds like tetralone[1] and 1-keto-tetrahydrophenanthrene[2] should be investigated.

Summary

1. An attempt to duplicate in vivo dehydrogenation of cyclohexane carboxylic acid by the use of dog's liver, pancreas, and kidney extracts has been unsuccessful.

2. No evidence of aromatization of cyclohexanol, cyclohexanone, Δ^2 cyclohexenol, and Δ^2 cyclohexenone was observed by the action of liver, pancreas, and kidney extracts.

3. A modified method for the preparation of Δ^2 cyclohexenone has been presented.

4. Suggestions for further investigation have been made.

STUDIES IN THE SYSTEM, LANTHANUM-HYDROGEN

Introduction

The earliest investigation of the lanthanum-hydrogen system worthy of mention is that conducted by Muthmann and Kraft[3] in 1902. The metal was prepared by electrolysis of lanthanum chloride in a copper vessel fitted with carbon electrodes. In the preparation of the hydride the metal was placed in a porcelain or copper boat and the hydrogen used was made by the action of zinc on sulfuric acid. The hydrogen was purified by passage through ammoniacal silver nitrate solution, alkaline and acid permanganate, alkaline pyrogallol and finally, sulfuric acid. The amount of hydrogen absorbed by the metal was determined by weighing the sample of metal before and after reaction with hydrogen. The percentages of hydrogen absorbed by different samples were 1.98, 1.84, 1.83, 201, and 2.10. The average of these values is 1.95. The percentage of hy-

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[1]This contains one ring already aromatized. It has been suggested that the presence of one aromatic ring tends to accelerate the aromatization of adjacent rings: viz., the ready transformation of equilin to equilenin.

[2]This compound is oestrogenic.

[3]Muthmann and Kraft, Ann., 325, 261 (1902).

drogen required for the formula LaH_3 is 2.12%.

The measurement of the dissociation of lanthanum hydride, conducted by Muthmann and Baur,[1] gave results which were not reproducible and pressures which changed with time. The authors concluded that lanthanum hydride formed no compound of definite composition.

Sieverts and Müller-Goldegg[2] used lanthanum mischmetal consisting of 10.2% cerium, 84.3% lanthanum and small amounts of neodymium, praesodymium, iron, aluminum and silicon. The metal was placed in a magnesia container and the hydrogen was prepared by the electrolysis of dilute sulfuric acid and purified through palladium. It was observed that the metal absorbed hydrogen readily at room temperature to yield a lead gray powder. Other experiments in which the metal was first heated to 870° in vacuum yielded the same type of hydride. An average[3] absorption of 220.1 cc. per gram which corresponds to 1.94% of hydrogen by weight, was reported. In later experiments, by Sieverts and Roell,[4] commercial hydrogen from steel containers and containing no catalytic poisons, was allowed to react with the lanthanum mischmetal and an absorption of 211.7 cc. per gram resulted. A number of experiments were conducted with cerium mischmetal and the absorption of hydrogen using commercial hydrogen was different from that when the electrolytic hydrogen of Sieverts and Müller-Goldegg was used.

In the dissociation experiments of Sieverts and Müller-Goldegg, most of the readings were taken after they had remained constant for fifteen minutes. The equilibrium was approached from both sides and reasonably consistent results were obtained. A pressure-composition curve (at 800°) showed three distinct parts. Part one rose gradually, part two was almost horizontal and part three rose rapidly. The authors suggested that the lanthanum-hydrogen system was similar to the palladium-hydrogen system.

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[1] Muthmann and Baur, Ann. 325, 266 (1902).

[2] Sieverts and Müller-Goldegg, Z.anorg. alleg. Chem., 131, 65 (1923).

[3] A volume method for estimating the hydrogen was used in an apparatus described by Sieverts and Hagenacker, Z. physik.Chem., 68, 116 (1909).

[4] Sieverts and Roell, Z. anorg. alleg. Chem., 146, 149 (1925).

In the dissociation experiments of Sieverts and Roell, most of the determinations were conducted above 800° while in the work of Sieverts and Müller-Goldegg most of the determinations are conducted below 800°. It is therefore difficult to make a comparison between the two. In the work at 1100°, the isotherms were not reproducible but are distinguished from the three part isotherm at 800° in that the curves are continuous from the saturation point to the hydrogen-free metal.

The impurity of the lanthanum sample used by all of the afore mentioned investigators, and the possibility of interaction with the container at high temperatures cast considerable doubt on the reliability of all the lanthanum-hydrogen studies to date. The generous gift of a number of rare earth elements to Dr. Warren C. Johnson by Professor B. S. Hopkins and Dr. L. F. Audrieth of the University of Illinois has enabled a re-investigation of the lanthanum-hydrogen system.

Apparatus and Materials

Purification of hydrogen.--Electrolytic hydrogen of commerce was purified by diffusion through a heated palladium tube according to the procedure described by Kraus and Lucasse.[1] The hydrogen purification apparatus was found to operate most efficiently at a temperature of approximately 450°.[2]

Apparatus for the formation and dissociation of lanthanum hydride.--The apparatus, shown schematically in Figure II, consisted of a means of storing hydrogen obtained from the palladium diffusion tube, a reaction tube, a manometer and a means of evacuating the system.

The stopcock A opened into a system consisting of a McLeod gauge, a mercury vapor pump and a Cenco Hyvac oil pump. Stopcock B and R opened to the hydrogen storage bulbs which were connected to the hydrogen diffusion apparatus through stopcock H. A fused quartz reaction tube, fitted with a ground glass joint at J, opened into the rest of the system through stopcock D. In order to place a Chromel-Alumel thermocouple element T as near as possible to the

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[1] Kraus and Lucasse, J.A.C.S., 44, 1941 (1922).

[2] Sidwell, Ph.D. dissertation, University of Chicago, Department of Chemistry, 1934, p. 11.

reaction region, the wires were sealed through the lower portion of the female part of the ground joint. In the reaction tube, the wires were contained in a two-hole alundum tube. Stopcock M allowed the manometer to be re-evacuated from time to time.

The furnace F was arranged in such a manner as to be moved horizontally from the reaction tube. It was heated by 110 volt A. C. and maintained at constant temperature for a particular setting of the external resistances by the use of ballast tubes.[1] A Type K, Leeds-Northrup, potentiometer was used in the measurement of the E.M.F. developed by the Chromel-Alumel thermo-couple.

The smaller of the two bulbs S, was always used when adding hydrogen to the metal. Its volume was determined by weighing empty and then full of water. The volume of the section between stopcocks[2] A, B, R, D, H, and C, and the volume of the reaction tube was determined by expansion from the bulb of known volume. The volume of the manometer tubing was determined by weighing a a ten centimeter length, full of mercury.

Experimental

The possibility of interaction of the rare earth elements with metal and porcelain containers eliminated these as suitable containers for the rare earth sample. To determine the advisability of the use of alundum or magnesia[3] containers, samples of mischmetal (95% cerium) were heated therein to 700° in vacuo. The molten cerium flowed into the pores of the containers but no visible reaction took place. Cerium hydride, prepared at 400°, also showed no interaction. However, the heating and cooling of the sample in these containers caused them to crack and it was decided that a small clear quartz test tube should be used as the container and that this study should be conducted below 500°. Under these conditions, no interaction was observed between the lanthanum (or the yttrium[4]) and the quartz tube.

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[1] Jones, Gen. Elec. Rev., 28, 329 (1925).

[2] This section will hereafter be referred to as the "stopcock enclosed section."

[3] The author wishes to thank Dr. Lyle Hill for his gift of a 99.9% magnesium oxide tube.

[4] A powdered sample of yttrium was placed in the reaction system previously described and no reaction with hydrogen at a pressure of 33.8 cm. took place at room temperature or upon heating to 650° and subsequent cooling.

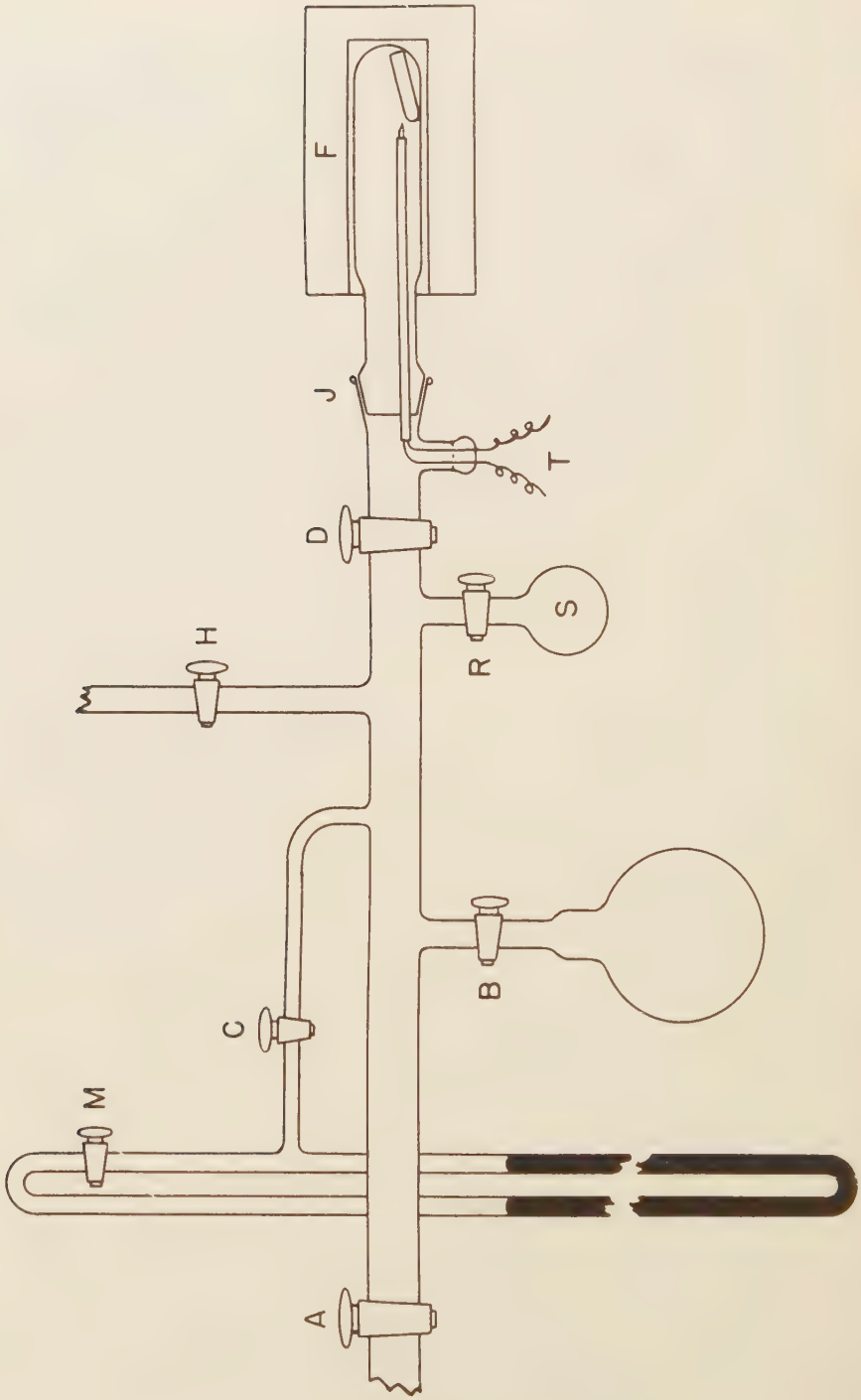

Fig. 2

A. Formation of Lanthanum Hydride

A sealed glass tube containing the pellets of lanthanum was opened in a dry-box through which was passing a stream of dry carbon dioxide. The sample was transferred to the previously weighed quartz test tube and corked. This was then placed in an ordinary test tube and corked. The lanthanum, thus maintained in an atmosphere of carbon dioxide, was removed from the dry box. The corked quartz test tube was taken out of the larger tube and rapidly weighed. It was then rapidly replaced in the dry box and uncorked. After having been pushed into the quartz reaction tube with a glass rod so that the open end of the quartz test tube faced the closed end of the quartz reaction tube, the latter was corked prior to removal from the dry box. Upon removal from the dry box, the reaction tube was immediately connected to the rest of the vacuum system and evacuated. The temperature was raised to 200° while continuously pumping. The thermocouple wires now faced the closed end of the quartz test tube containing the lanthanum. The possible contamination of the sample by the wires was thereby eliminated.

After cooling to room temperature, this 0.5258 gram sample was subjected to a pressure of 34.9 cm. After seven hours, the pressure had dropped to 0.2 cm. The pressure was then increased to 35.2 cm. which fell to 20.3 cm. in two hours and stayed at this value for twelve hours. During the reaction with hydrogen, the lanthanum crumbled to a gray-black powder. Since the lanthanum was not absorbing more hydrogen, hydrogen was added in order to establish an increased pressure of 51.8 cm. This increase in pressure did not result in more absorption. The temperature was raised to 495° over a period of five days. The pressure increased to 59.9 cm. and remained at this value for sixteen hours. This pressure was greater than that expected from the expansion of the hydrogen. After cooling to room temperature over a period of seven hours, a pressure of 49.9 cm. remained.

The volume of hydrogen absorbed at room temperature, reduced to standard conditions, was 100.7 cc. This corresponded to 191.7 cc. per gram which yielded a formula of $LaH_{2.37}$. If the volume associated with the two centimeter decrease in pressure due to the heating and cooling of the sample was taken into account, a total absorption of 103.1 cc. took place. For one gram, this amounted to 196 cc. and corresponded to a formula of $LaH_{2.43}$.

(Sievert's formula is approximately $LaH_{2.8}$.) For a formula of LaH_3, one gram of lanthanum should have reacted with 242 cc. of hydrogen.

Attempt to determine equilibrium pressures.--Stopcock R was closed and the reaction tube, the enclosed stopcock section and the manometer were evacuated at room temperature. After closing stopcock A, the temperature was raised to 103° over a period of four hours. A pressure of 0.6 cm. built up and remained constant for five hours. This hydrogen was pumped out and after ten hours a pressure of 0.2 cm. built up. After removal of this hydrogen, the temperature was further increased and the corresponding pressures are shown in Table 1.

TABLE 1

DISSOCIATION PRESSURES OF THE LANTHANUM-HYDROGEN SYSTEM

Temperature (°C.)	Pressure (cm.)	Time (hrs.)
100	0.0	0
151	0.9	2
176	1.6	3
197	2.4	4
250	5.0	5 1/2
309	8.9	8
345	11.6	10
376	13.9	12
382	14.7	24 1/2
382	14.7	26
382	14.5	30
382	14.5	31
378	14.2	36 1/2
379	14.4	50
381	14.5	51
378	14.3	52
377	14.2	57

The enclosed stopcock section was evacuated and the pressure was thus decreased to 10.7 cm. The pressure then increased to 11.4 cm. and after twenty-four hours,[1] the enclosed stopcock section was again evacuated, and a new pressure of 9.0 cm. was established. Over a period of nineteen hours, this pressure did not increase. This procedure of evacuating the stopcock section and thereby reducing the pressure in the system was repeated until a pressure of 0.2 cm. was reached. Throughout this series of determinations, as a new pressure was established, it remained at this

[1]Slight fluctuations were observed during the twenty-four hour period.

value. This procedure was again followed at 520° and with the same result. At this point, a total of ten cubic centimeters of hydrogen had been removed.

The hydrogen bulb S was now opened, and approximately 13 cc. of hydrogen were immediately absorbed. The pressure was 29.3 cm. The sample was cooled to room temperature over a period of two days and 10 cc. of hydrogen were taken up. At room temperature the pressure was increased to 54.7 cm. but no further reaction took place.

Once again, the lanthanum hydride was heated in the evacuated system consisting of the reaction tube, the enclosed stopcock section and the manometer. Pressures consistent with those obtained previously were observed up to 280°. At this temperature, the pressure increased to 59.2 cm. in six days. It was suspected that there was a leak in the system. The system was cooled to room temperature over a period of an hour and a half and a final pressure of 51.9 cm.[1] remained constant for twelve hours. It was apparent that this continued increase in pressure was not the result of a large leak in the system. The temperature was again raised to 280° over a period of three days. After twenty-six hours at this temperature, a pressure of 65.5 cm. was reached which remained constant for twenty-four hours. The temperature was gradually raised to 500° and the pressure increased accordingly.

Due to improper temperature control, the temperature accidentally rose to about 850° and the investigation on this sample was discontinued. However, it was again observed that the lanthanum, on cooling, did not reabsorb the hydrogen.

B. Formation of Lanthanum Hydride

The procedure[2] for introduction of the sample, etc., was the same as for Sample A. An initial pressure of 49.6 cm. acting on a 0.4827 gm. sample decreased to 3.6 cm. in two hours. When

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[1]Evidently, the hydrogen did not recombine with the metal.

[2]A new quartz reaction tube was used. When it was heated to 300° with no sample present, a decrease in hydrogen pressure was continuously observed. At room temperature, this phenomenon did not take place. A glass reaction tube did not exhibit this peculiarity and it was therefore used in this second study. The sample itself, however, was placed in a small quartz test tube as described in the experiments on the first lanthanum sample.

more hydrogen was added to establish an increased pressure of 50.5 cm., a final value of 49.8 cm. was reached in six hours. The temperature was raised to 400° and subsequently cooled, but no further reaction occurred. The sample had reacted with 94.6 cc. of hydrogen. This corresponds to 196 cc. per gram and a formula of $LaH_{2.43}$.

Attempt to determine equilibrium pressures.--Stopcock R was closed and the reaction tube, the enclosed stopcock section, and the manometer were evacuated at room temperature. The temperature was then raised and the pressures observed are shown in Table 2.

TABLE 2

DISSOCIATION PRESSURES OF THE LANTHANUM-HYDROGEN SYSTEM

Temperature (°C.)	Pressure (cm.)	Time (hrs.)
23	0.0	0
94	1.1	1/2
120	2.0	1 1/2
134	2.3	3 1/2
135	2.3	15 1/2
135	2.3	16 1/2
172	3.5	19
195	4.3	19 1/2
218	5.5	21
275	8.6	25 1/2
281	9.0	29
280	8.8	39
307	11.0	43
316	29.1	49
316	32.6	50
316	65.9	63 1/2
315	75.6	75 1/2

This pressure increase would have continued but since the apparatus could measure only one atmosphere, the stopcock section was evacuated and a new pressure of 56.9 cm. was established. After thirteen hours the pressure rose to 62.9 cm. In another three hours, the pressure rose to 63.1 cm. After remaining constant at 63.1 cm. for ten hours, the stopcock section was again evacuated and the pressure thus decreased to 47.2 cm. The pressure increased to 66.0 cm. in thirty-four hours and stayed at this value for twelve hours. By removing the hydrogen in the stopcock section, the pressure was decreased to 49.5 cm. It increased over a period of two days to 67.6 cm. and stayed constant for twenty-four hours.

The reaction tube was cooled to room temperature but no hydrogen was reabsorbed over a twenty-four hour period. The temperature was again increased to 318°; the hydrogen in the stopcock section, reaction tube and manometer was pumped out and in twelve hours, a pressure of 1.4 cc. built up. There was no further increase in seven hours. This 1.4 cm. was removed and after nineteen hours, a 0.4 cm. pressure was observed.

After a constancy of eight hours, this 0.4 cm. of hydrogen was pumped out and the temperature was lowered to 140°. No pressure built up within eleven hours. In order to follow up the possibility that a retransformation to the form of lanthanum that reacted with hydrogen might take place at a lower temperature, the sample was left under a pressure of 44.9 cm. at 140° for thirty hours. A decrease of a few millimeters took place but such small changes were within the magnitude of error of the determination and have often been due to changes in room temperature. Upon cooling to room temperature, no reaction took place.

Discussion

The method of preparation, the susceptibility to oxidation, the method of activation and the state of subdivision are among the variables which must be considered in this type of reaction. Hence, no comparison between the formula $LaH_{2.4}$ found in this investigation and the formula $LaH_{2.8}$ found by Sieverts can be made. It should be recalled that Sieverts used an 85% lanthanum mischmetal.

The obvious lack of any true equilibrium pressure repeatedly observed in this study is in marked contrast to the work of Sieverts in which reasonably consistent pressures were reported. In Sample A, in the first attempt to determine equilibrium pressures (Table 1), a fairly good straight line was obtained when the logarithm of the pressure was plotted against the reciprocal of the absolute temperature, but any suggestion of reproducibility was completely negated by the observation thereafter. An interesting anomaly occurred in the attempt to determine equilibrium pressures when working with the second sample of lanthanum hydride. A pressure of 63.1 cm. remained constant for twenty-four hours and was then decreased to 47.2 cm. When a new "constant" value was established, it was found to be 66.0 cm. which corresponded to an over all three centimeter increase. This pressure of 66.0 cm. was

reduced to 49.5 cm. After some time, a new pressure of 67.7 cm. resulted. A possible interpretation is that as more hydrogen is removed, the lanthanum changes to the form which is incapable of reacting with hydrogen. This may be associated with a transformation in the lattice which forces more hydrogen out.

The inability of the lanthanum, from which some hydrogen has been removed, to recombine with this hydrogen suggests that there are two forms of lanthanum. In the work of Sieverts and Müller-Goldegg, a specific instance of a change in reactivity is mentioned for cerium, but the magnitude is not as great as observed herein. These authors cite that cerium mischmetal had reacted with 216 cc. of hydrogen. After having been heated twice to 750° and cooled, it was found to absorb only 164 cc. An X-ray study of lanthanum, prior to reaction with hydrogen and after removal of hydrogen, would prove of considerable interest.

Summary

1. Lanthanum reacts readily with hydrogen at room temperature to give an approximate formula of $LaH_{2.4}$.

2. No reproducible equilibrium pressures are found.

3. Some evidence for the existence of two forms of lanthanum is presented.